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Trace Organics Removal Using Activated Carbon and Polymeric Adsorbents

Iowa State Univ.
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Prepared for

Municipal Environmental Research Lab.
Cincinnati, OH

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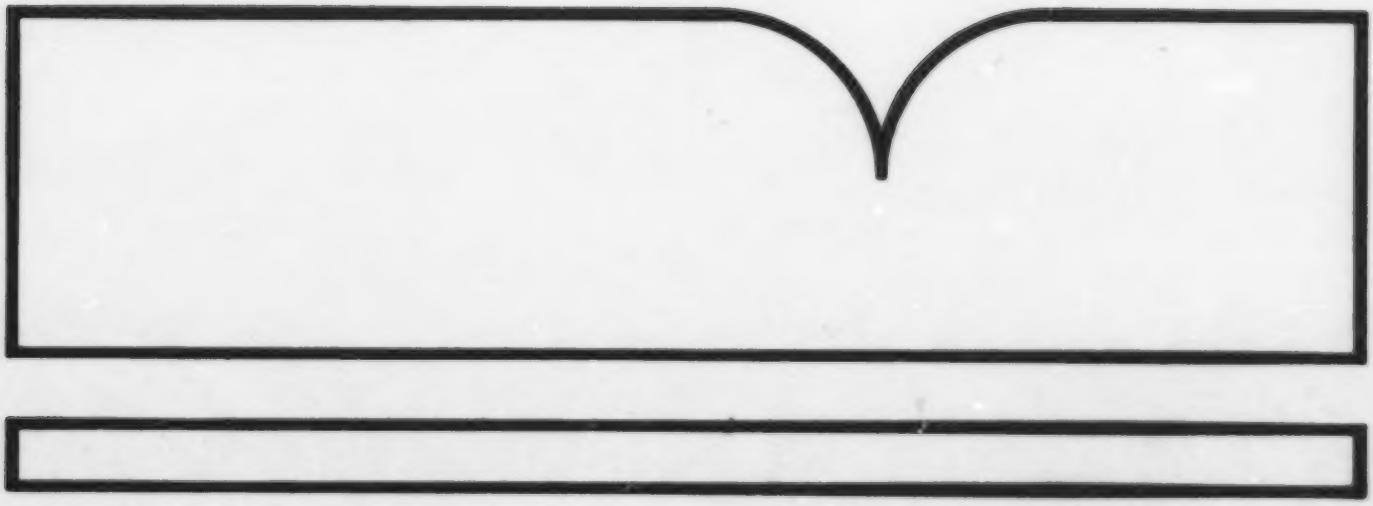

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TRACE ORGANICS REMOVAL USING ACTIVATED CARBON AND POLYMERIC ADSORBENTS

by

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Grant No. R-804433

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This study was conducted
in cooperation with the
American Water Works Association
Research Foundation
Denver, Colorado 80235

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U.S. ENVIRONMENTAL PROTECTION AGENCY
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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the research and the user community.

Low but potentially significant concentrations of organic matter in water including known and suspected carcinogens have stimulated the investigation of a variety of adsorbents capable of removing these compounds from water. Part Three of this report summarizes the results of laboratory and pilot plant tests conducted with a variety of adsorbents that might be selected for trace organics removal.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

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ABSTRACT

A survey of trace organic matter in 14 water supplies was conducted and an investigation was made to compare the effectiveness of granular activated carbon with polymeric adsorbents for removing the trace organic matter from one of these water supplies. The study was conducted in three parts by three universities.

The water quality survey was conducted by the Ames Laboratory at Iowa State University to determine monthly concentrations of trihalomethanes and TOC, as well as the occurrence of selected organic compounds listed in the Federal Register and mutagenicity as measured by the Ames test. Most of the water supplies tested should be able to meet trace organics requirements with conventional treatment methods.

Bench scale tests were conducted at the University of Illinois-Urbana to select a granular activated carbon and a polymeric adsorbent for side-by-side comparison in a pilot plant at the Kansas City Missouri Water Treatment Plant. The pilot plant was operated by the University of Missouri-Columbia. The pilot plant tests demonstrated that the kinds of granular activated carbon that are used in water supply applications are capable of removing organic matter covering a wide range of molecular weights. The polymeric resins were much more limited in the range of organic matter they would remove.

This report was submitted in fulfillment of Contract No. R804433 by Iowa State University under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period May 1976 to November 1978 and work was completed as of April 1980.

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The contributions of Dr. C. D. Chriswell, Mr. G. A. Junk, Mr. J. J. Richard, Dr. J. S. Fritz, Dr. H. J. Svec, Dr. M. D. Arguello, and Dr. B. A. Glatz for the development of analytical methods and for the conduct of the analytical procedures are acknowledged. The efforts of Dr. E. R. Baumann for selling the AWWA Research Foundation on the idea that the project should be initiated, of Mr. E. F. Spitzer for crganizing the financial and technical support for the project, and of Mr. M. J. Taras in providing patient and highly professional project management are also acknowledged. Dr. V. L. Snoeyink and Dr. J. T. O'Connor are gratefully acknowledged for agreeing to be a part of a project of this kind, for shaping the way that the project developed, and for getting the job done.

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SECTION 1

INTRODUCTION

In January 1975 the AWWA Research Foundation listed fifteen high-priority problems warranting study. Included among these problems were two related to organics in drinking water. One problem was called "Reliable Screening Tests and Techniques for the Determination and Evaluation of Organics in Drinking Water." The other problem area was called "Method for Removal of Organics in Drinking Water."

At the time the list was published in 1975, widespread publicity was being given by the news media to the fact that drinking water supplies in many communities contained organic compounds that were not being removed by conventional water treatment processes. Furthermore, chlorine used in disinfection was demonstrated to be capable of changing compounds that are considered to be harmless into others that are considered to be carcinogenic.

The AWWA Research Foundation, therefore, authorized the initiation of a research project to investigate these two related problems on their list. During the summer of 1975, Elroy Spitzer, representing the AWWA Research Foundation, met with E. Robert Baumann and Charles Oulman at Iowa State University to outline the scope of a research proposal that could be submitted by the AWWA Research Foundation to its membership and to the EPA for funding. The research project was funded by the Municipal Environmental Research Laboratory (EPA), fourteen water utilities, and the AWWA Research Foundation.

The effort in the project was divided into three parts to be carried on concurrently on three separate campuses. One part of the project was a survey of trace organics in the water supplies of the fourteen participating water utilities. This survey was conducted by the Ames Laboratory at Iowa State University with Harry J. Svec and James S. Fritz as co-project leaders. A second part of the project was bench-scale studies to select adsorbents for use in a pilot plant. These studies were conducted in the Department of Civil Engineering-Urbana at the University of Illinois. Vernon L. Snoeyink was the project leader. The third part of the project consisted of pilot plant tests comparing treatment using activated carbon with polymeric adsorbents at the Kansas City Water Treatment Plant. The pilot plant was designed, fabricated, and operated by personnel from the University of Missouri-Columbia. John T. O'Connor was the project leader for the pilot plant tests. Project coordination was provided by Charles Oulman, Department of Civil Engineering at Iowa State University, who served as the principal investigator.

The final report for the project is being submitted in three parts. Part 1 by Vernon L. Snoeyink et al., is entitled BENCH SCALE EVALUATION OF RESINS AND ACTIVATED CARBONS FOR WATER PURIFICATION. Part 2 by John T. O'Connor et al., entitled THE REMOVAL OF TRACE ORGANICS FROM DRINKING WATER USING ACTIVATED CARBON AND POLYMERIC ADSORBENTS, provides the technical details relating to the pilot plant tests. This third and final part of the report will provide an overview of the results obtained in the entire project including each of the three study areas.

SECTION 2

CONCLUSIONS

Trace amounts of organic matter in drinking water have become a source of public health concern because of the potential hazard that is associated with some of the compounds such as chloroform. The finished water from each of the water utilities surveyed contained measurable amounts of a number of organic compounds that have been listed in the Federal Register. Significant levels of the various trihalomethanes were also found in the finished water from each supply but not at levels that would necessitate treatment in most of the water supplies. Mutagenic activity in the finished water was also indicated in over half of the water supplies.

Control of trace organic matter by water treatment methods could involve the use of adsorbents such as activated carbon or polymeric adsorbents. It was demonstrated in this study as it has been in other studies that granular activated carbon will remove trace organic matter ranging from low molecular weight compounds such as chloroform to high molecular weight compounds such as humic acids. Polymeric adsorbents were found to be much more selective in the range of organic compounds that they can adsorb.

Even though an adsorbent such as granular activated carbon has a reasonably high capacity, the efficiency of adsorption may be low depending on the bed depth, the flow rate, and the influent concentration of trace organic matter. A 3-ft bed of activated carbon was deep enough with an empty bed contact time (EBCT) of only 11.2 min to obtain about 90 percent utilization of the capacity of the adsorbent for removing the total trihalomethanes (TTHM) from water for an adsorption bed run to 50 percent breakthrough. The efficiency of the same activated carbon was less than 60 percent for removing total organic carbon (TOC) when the adsorption bed was run to 50 percent breakthrough. In these cases concentration was the key factor--the influent concentration of TTHM was about 40 µg/l whereas the concentration of TOC was about 3 mg/l, almost 100 times as high.

The general conclusions of this study are that trace organic matter significant to public health was present in all of the water supplies tested although not necessarily at concentrations that pose a health hazard, and that the kinds of granular activated carbon used in water supply applications are capable of removing this organic matter from water. Polymeric adsorbents and some special grades of activated carbon had a high capacity for trace organic matter also but the range of molecular weight compounds they can remove is extremely limited. The specific conclusions of this study are:

1. TTHM concentrations were low enough in 13 of the 14 water utilities that were surveyed so that a 100 µg/l standard can probably be met with conventional treatment methods.

2. The best quality water with respect to TTHM concentrations came from a protected well. Water from lake sources was the next best, followed by impounded water and river water. The lowest quality water supply with respect to TTHM concentrations was a shallow well from an aquifer subject to surface sources of contamination.

3. Mutagenic activity as measured by the Ames test was found in the finished water from 8 of the 14 water utilities. Plasticizers listed in the Federal Register were found in the finished water of each of the utilities. These contaminants do not necessarily indicate that the water poses a health hazard, but these results do indicate that man-made organic chemicals are present and that potentially carcinogenic materials may be found in most of the water supplies.

4. The three water grade activated carbons that were tested to select a carbon for use in the pilot plant tests were nearly equivalent to each other and the choice of which carbon should be used was practically an arbitrary one. The relative effectiveness for the removal of methylisoborneol (MIB) in the presence of humic acid was 135, 100, and 95 respectively for Westvaco WVG, Calgon Filtrasorb 400, and ICI HD 4000. For humic acid removal the relative effectiveness was 110, 100, and 75 respectively for ICI HD 4000, Calgon Filtrasorb 400, and Westvaco WVG. If equal weight was given to humic acid and MIB removal, the average relative effectiveness would have been 105, 102.5, and 100 respectively for Westvaco WVG, ICI HD 4000, and Calgon Filtrasorb 400. Westvaco WVG was selected for use in the pilot plant because of its good capacity for both humic substances and MIB.

5. None of the resins tested could be recommended to be used by itself in the pilot plant tests. Therefore, it was necessary to select two materials that could be used as a combination in series. A phenol-formaldehyde resin with a relative effectiveness of 75 for humic acid removal and 0 for MIB removal and a carbonaceous resin, Rohm and Haas XE 340, with a relative effectiveness of 50 for MIB removal and 0 for humic acid removal were the two materials chosen. Two 3-ft beds of Diamond Shamrock ES-561 followed by one 3-ft bed of XE 340 were compared on a side-by-side basis with three 3-ft beds of Westvaco WVG. Based on a weighted average for the two kinds of trace organic matter and the bed lengths, the average relative effectiveness was 33 for the resin combination compared with 105 for the activated carbon.

6. The run length in each of the four phases of the pilot plant study was too short to challenge more than about 3 ft of bed depth of the water grade carbons and the XE 340 resin for TTHM removal. The relative effectiveness of these adsorbents for TTHM removal was

167, 133 and 100 respectively for the XE 340 (resin), the ICI HD 1030 (a lignite base carbon) and Westvaco WVG (a bituminous base carbon). The highest relative effectiveness found was 225 for the performance of the Calgon carbon selected for enhanced trihalomethane removal.

7. The best all around performance for all of the adsorbents tested was obtained with an extruded peat base activated carbon. Based on equal weights for TTHM and TOC removal, the relative effectiveness of the various adsorbents that could remove both TOC and TTHM was 147, 100, 96 and 88 respectively for American Norit ROW 0.8, Westvaco WVG, Union Carbide LCK (a petroleum base carbon) and ICI HD 1030.

8. Regeneration was effective in restoring the capacity of each of the adsorbents that was put through several cycles of use in the pilot plant.

9. The capacity, N, of the adsorbents varied with the concentration, C, of the organic matter in the water. The equation for a Freundlich isotherm correlated capacity-concentration results for both the adsorption isotherm test results in the bench scale studies and the TTHM uptake results on WVG carbon in the pilot plant tests. As a rule of thumb, the capacity of activated carbon was approximately proportional to the square root of the concentration of the solute being removed:

$$N = k\sqrt{C}$$

Thus, by doubling the concentration of solute in the water being processed, the capacity of the activated carbon is increased by about 40 percent.

10. The efficiency of an activated carbon for utilizing the adsorption capacity for TTHM was very good, in part because the concentration of TTHM in the water was very low. The efficiency for removing TOC was very low compared with the efficiency for TTHM removal, in part because the TOC concentration was so much higher than the concentration of TTHM. Effectively, much of the organic matter contributing to TOC was harder to adsorb than TTHM.

11. The threshold odor number (TON) for the water tested in the pilot plant was so low that it was not possible to determine whether the various adsorbents would be effective in removing TON from the water supply. It appeared that the adsorbents did tend to degrade the water quality somewhat with respect to TON when a fresh bed of adsorbent was put into operation.

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SECTION 3

RECOMMENDATIONS

1. The water grade carbons that were evaluated in the bench scale and the pilot plant studies performed adequately for the removal of organic matter covering a wide range of molecular weights; resins were much more limited in the range of organic matter that they would remove. Therefore, unless the number and type of organic compounds to be removed is relatively limited, activated carbon is recommended as the adsorbent of choice in a water treatment application.

2. In selecting the adsorbents to be used in the pilot plant, humic acid and MIB removal was used as the criterion for evaluating available materials. In the pilot plant, the parameters used in evaluating performance included TOC and TTHM. The parameters measured in the pilot plant were site specific and varied from day to day. The parameters used in the bench scale tests probably do not represent very closely the kinds of organic matter actually present in a particular water supply. Methods for concentrating organic matter out of the water being treated in a given water utility and a rational basis for weighting the results of measurements of the adsorption capacity for the selected components of that organic matter need to be worked out. It is recommended that more research effort be directed toward the establishment of criteria and a protocol for screening adsorbents using the adsorption isotherm test and organic matter found in the water to be treated.

3. The efficiency of adsorption beds depends on the shape of the breakthrough curve that develops for the range of materials scheduled for removal. If the breakthrough curve is very steep, a single bed with a relatively short EBCT is appropriate. If the breakthrough curve is very flat, several beds operated in series will increase the efficiency of adsorption provided that the first bed in the series is regenerated when the water leaving the last bed reaches the selected effluent quality. In the design of adsorption beds for water treatment applications it is recommended that multiple bed designs be considered as well as single bed designs and that the efficiency of utilizing the capacity of the adsorbent be specifically considered in selecting the best design alternative.

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SECTION 4

WATER QUALITY SURVEY

PARTICIPATING UTILITIES

Fourteen water utilities participated in the water quality study both financially as well as in the collection of samples for analysis. The water utilities were scattered across the United States. Four were located on the West Coast--two in the San Francisco area and two in Southern California. The other ten water utilities were located in the Eastern half of the country --two in the Midwest, two in the Ohio River Valley, one on one of the Great Lakes, two in New England, one in the Middle Atlantic States, and two in the Southeast.

Most of the supplies were surface water supplies. Several were lake water supplies, several utilized impoundments, and about half depended on direct draft from a large river. Two supplies utilized both well water and direct draft from a surface source.

All of the water supplies were disinfected by chlorination and all but one of the supplies was a filtered water supply. The forms of treatment employed in the various treatment plants included lime softening, chemical coagulation, treatment with powdered activated carbon, and treatment with granular activated carbon.

By and large, most of the communities served by the water utilities participating in the water quality survey were large or were in large metropolitan areas. The laboratory facilities available were generally very good. Several of the laboratories are equipped with specialized equipment for the monitoring of trace organic compounds, and most of the utilities have staffed their laboratories with highly trained and skilled analysts capable of performing the trace organics analyses themselves. Some of the water utilities are carrying on research independently to solve water quality problems of local interest.

Analysts from each of the participating water utilities met in Ames in May 1976 to get acquainted with the analysts at Iowa State University who would be working up the samples collected in the various water utilities and to get acquainted with the sampling techniques and analytical procedures that would be employed. When the analysts returned to their respective water utilities, they took along sampling kits for the collection of the first monthly sample. During the month of July, the principal investigator visited each of the water utilities to inspect the locations that had been

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selected for sampling of the raw, intermediate and finished water. As a result of the inspection made by the principal investigator, sample points were shifted to new locations in a number of systems.

Essentially, the raw water sample was intended to be collected before any treatment had taken place and certainly before any chlorine had been added which might lead to the formation of trihalomethanes. The intermediate sampling point was intended to show the effects of treatment primarily with limited, if any, contact time for the reactions with chlorine to have gone to completion. The finished water sample was intended to be taken in the system at a point that would be representative in providing a contact time with chlorine similar to that of water used by the typical consumer.

The sampling program used in this study was intended to extend over one full year so that seasonal variations in the occurrence of trace organic compounds would be apparent. The sampling program began in July 1976 and actually continued through August 1977 at two of the utilities, through September 1977 at eight, and through October at four of the utilities. Three of the water utilities submitted 8 samples, two submitted 9, two submitted 10, two submitted 12, two submitted 13, two submitted 14 and one submitted 15 samples.

ANALYTICAL METHODS

The analytical methods used in the water quality survey can be separated into three categories: procedures for trihalomethanes, procedures for gas chromatographable compounds collected by adsorption on activated carbon or on resins, and procedures for assaying the mutagenicity of compounds collected by adsorption on activated carbon or resins.

The trihalomethanes were determined by a solvent extraction procedure [1] in which the extract was analyzed with a gas chromatograph employing a flame ionization detector. Samples collected on the Carbon Resin Organic Compound Accumulators (CROCA Samplers) were eluted with ether and the extracts removed from both the activated carbon and the resin were chromatographed [2]. The total concentration of all gas chromatographable material removed from the CROCA Samplers was expressed in µg/l based on the response that the gas chromatograph detector gives for tridecane.

In addition, composite extracts were analyzed to determine whether a number of selected organic compounds listed in the Federal Register were present. Atrazine and Alachlor herbicides were selected because of their widespread use. Endrin and Heptachlor are insecticides that are a source of concern to the EPA and to the NAS. Because Heptachlor forms the epoxide in water, Heptachlor epoxide is the form sought in this study. Fluoranthene and acenaphthylene were selected as indicators of the presence of poly-aromatic hydrocarbons (PAHs) and coal tar contamination. These compounds may not pose a health hazard but their presence may indicate that other PAHs are present. Hexadecane was included as a typical alkane contaminant, 1-methylnaphthalene as a typical alkyl-substituted aromatic compound, and

1,2,4-trichlorobenzene as a representative chlorinated compound. The diethylhexylphthalate (DEPH) and the butylphthalalylbutylglycollate (BPBG) were chosen because they are common plasticizers often found in drinking water.

The mutagenicity of extracts from the CROCA samplers was determined using five different mutant strains of the Salmonella typhimurium bacterium. The mutagenicity assays were performed according to a procedure described by Ames, McCann and Yamasaki [3]. This is a bioassay which detects reverse mutations caused by organic compounds in which the bacterial strains used in the assay regain the ability to synthesize histidine--a function that was lost by the mutant strains used in the assay. The assay can be performed quickly, easily and inexpensively and it appears to be a reliable method for screening compounds to determine whether they are potentially carcinogenic.

ANALYTICAL RESULTS

The concentration of trihalomethanes in the finished water for each of the water utilities is shown in Figure 1. Water utilities 1, 3, 5, 6, 8, 10, and 11 are river water supplies; 2 and 4 are well water supplies; 7 and 9 are lake water supplies; and 12, 13, and 14 are impounded water supplies. The carbon/resin extract concentrations in the finished water are shown in Figure 2. Table 1 shows the indicator compounds that were identified in the finished water from each of the utilities. Figure 3 indicates the mutagenic activity that was found in finished water from each of the utilities using various strains of test organisms in the Ames Test.

The benefits of operating a well water supply as opposed to a surface water supply are dramatically illustrated in comparing the trihalomethane concentrations for water utilities 3 and 4. Water utility 4 derives its water from wells located along the same river supplying water to utility 3. Water utility 4 is downstream from water utility 3 so the water in the river in the vicinity of water utility 4 is probably of a lower quality than it is in the vicinity of water utility 3. Water utility 3 submitted eight "monthly" samples during a 13-month period extending from July 1976 through August 1977.

The total trihalomethane concentration for water utility 4 was less than 100 µg/1 throughout the study period and, with the exception of the samples taken from July through October 1976, the concentrations were less than 20 µg/1. These results support the statement relating to small public water systems in the Drinking Water Regulations [4]:

> "The impact of any regulations for organics will be especially great on small public water systems; those serving between 25 and 1000 or 10,000 persons. The installation, operation, and maintenance of some fairly sophisticated control processes and the monitoring requirements may result in very substantial per capita costs for small systems. EPA pointed out this problem in the Interim Drinking Water Regulations

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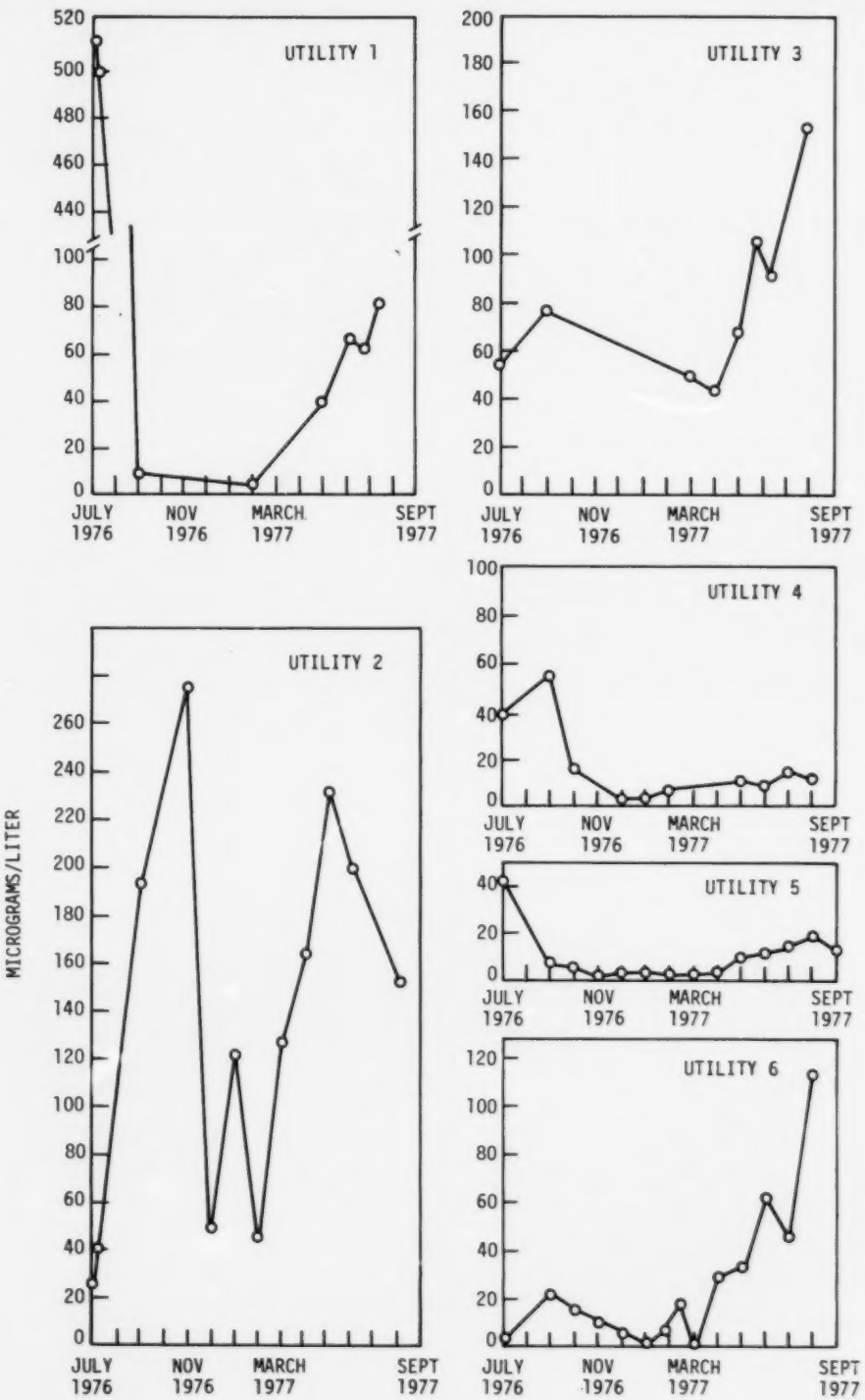

Figure 1. Trihalomethanes in finished water.

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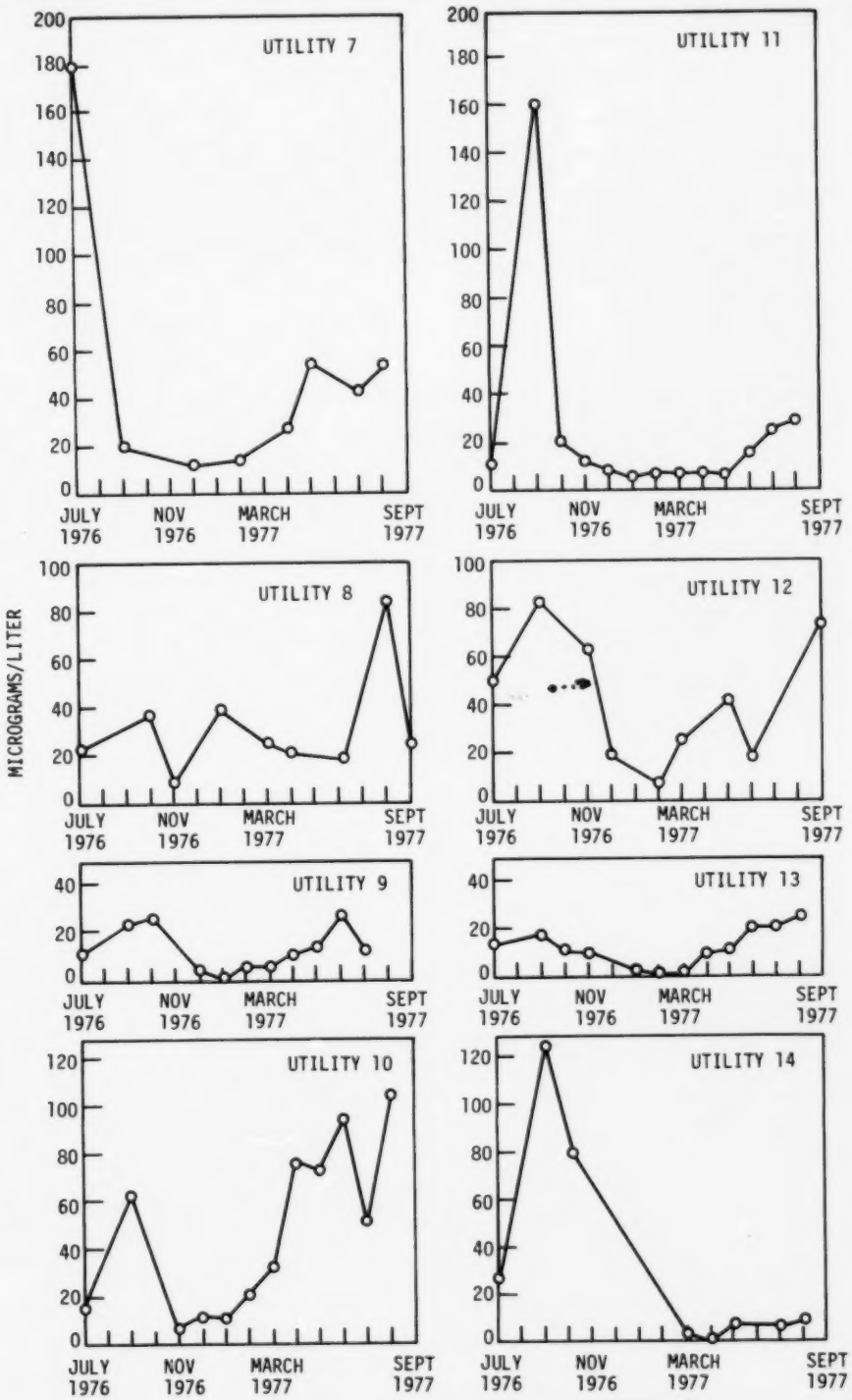

Figure 1 (continued). Trihalomethanes in finished water.

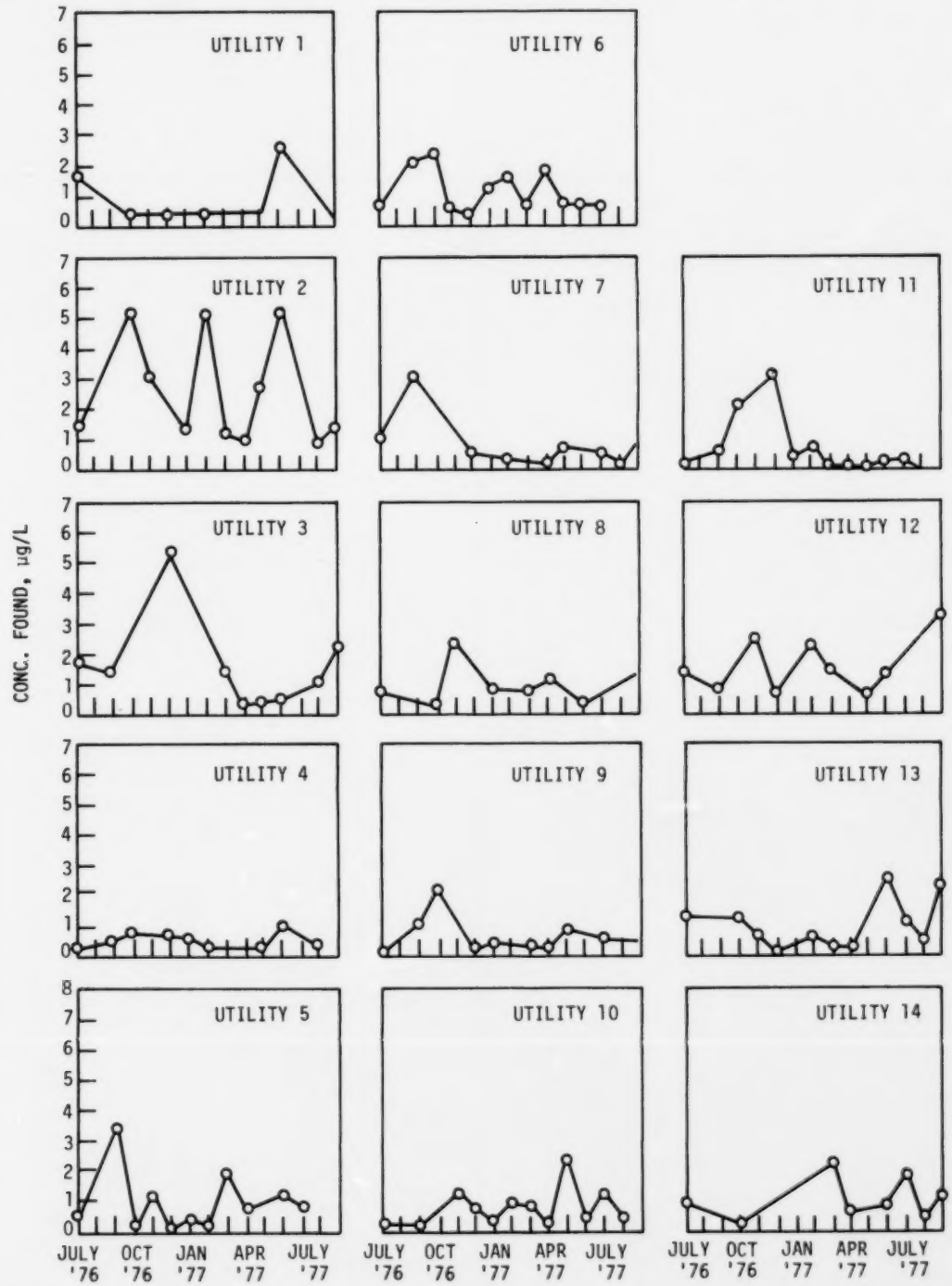

Figure 2. Carbon/Resin Extracts of Finished Water.

TABLE 1. INDICATOR COMPOUNDS IDENTIFIED

Compound	City 1	2	3	4	5	6	7	8	9	10	11	12	13	14
Atrazine	+	-	-	-	-	-	-	+	+	+	-	-	-	-
Alachlor	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Endrin	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Heptachlor epoxide	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Acenaphthalene	-	+	-	-	-	+	+	-	-	-	-	-	-	-
Fluoranthene	-	+	-	-	-	+	+	-	-	-	-	-	-	-
1-Methylnaphthalene	-	-	+	-	+	+	+	+	+	+	-	-	-	-
Hexadecane	-	-	-	-	-	-	+	-	+	-	-	-	-	-
1,2,4-Trichlorobenzene	-	+	+	-	-	-	-	-	-	-	-	-	-	-
Diethylhexylphthalate	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Butylphthalylbutylglycollate	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Nitrobenzene	-	-	+	-	-	-	-	-	-	-	-	-	-	-
Dibromochloromethane	+	-	+	+	+	+	+	+	+	+	+	-	+	+
Benzothiophene	-	-	-	-	-	-	-	-	-	-	-	-	+	-
Benzothiozole	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Triphenylphosphate	-	-	-	-	-	-	-	-	-	-	-	-	-	-

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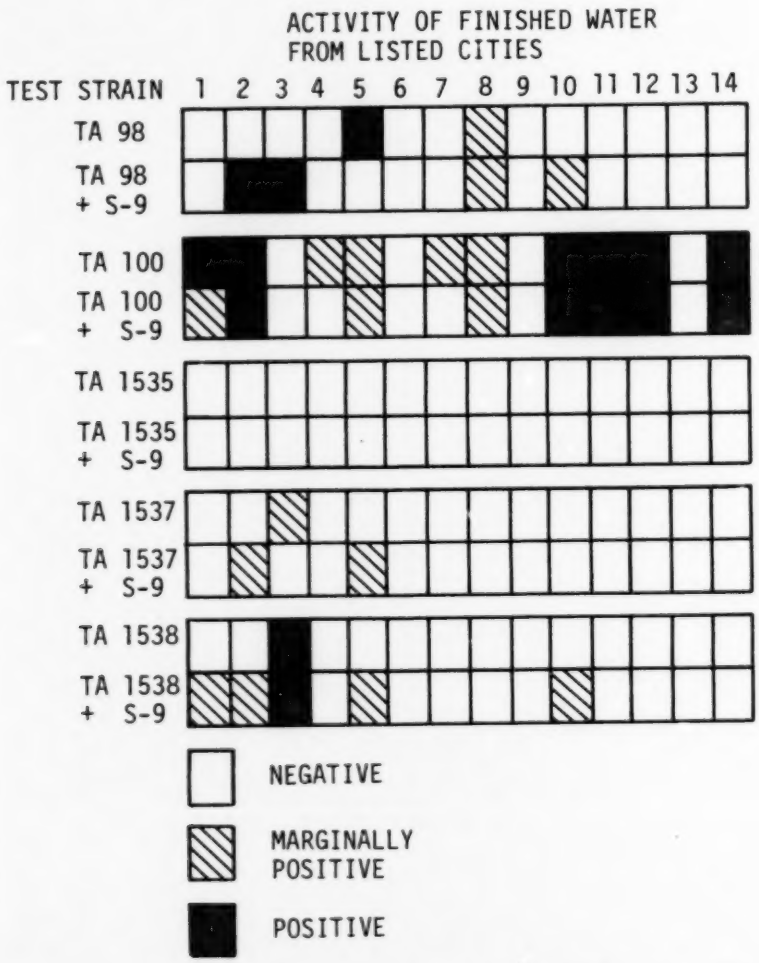

Figure 3. Mutagenic activity in finished water [5].

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and is seeking means of alleviating it. Fortunately many of those small systems utilize ground water sources which would not require extensive treatment. Since many ground waters are already low in organics, they also would produce very little chloroform (trihalomethane) and minimal, if any, treatment for organics control would be necessary in many cases. Thus the following regulatory options would likely impact primarily surface water supplies and shallow ground water sources."

The other ground water supply (Water Utility 2) obtains its water from a shallow and less protected source. The total trihalomethane concentration in the finished water for this water utility exceeded 100 µg/1 nine times during the period from July 1976 through September 1977. The carbon/resin extract concentrations were consistently higher in this water supply than in any of the others.

Only 18 percent of the finished water samples submitted from river water supplies contained a total trihalomethane concentration exceeding 100 µg/1. Based on the total number of months included in the sampling periods, those samples submitted represent 81 percent of the "monthly" samples that might have been submitted during the survey. Since 58 percent of the samples that were not submitted were wintertime samples when the concentration would probably have been much less than 100 µg/1, it is reasonably safe to assume that the concentration was less than 100 µg/1 more than 75 percent of the time.

Of the finished water samples submitted from the water utilities employing lakes as a source (Water Utilities 7 and 9), only one had concentrations exceeding 100 µg/1. That was the first sample submitted by that one utility, and it is possible that this one sample was not representative of the normal performance of that utility.

Only 7 percent of the samples submitted by the water utilities employing impoundments as a source (Water Utilities 12, 13 and 14) had trihalomethane concentrations exceeding 100 µg/1 and all of those were in one water supply. Of the three impoundments, the one serving water utility 13 appeared to be the best protected and this water utility had the lowest concentrations of trihalomethanes. The impoundment serving water utility 12 was reasonably well protected but the catchment area includes a substantial amount of boggy land. The impoundment serving water utility 14 is surrounded by agricultural areas that have caused the carryover of organic matter into the water source for many years. This water utility had the highest concentration of trihalomethanes of the three while their reservoir was in use.

In one of the treatment plants (Water Utility 6) powdered activated carbon was used as a treatment and in another (Water Utility 7) granular activated carbon was used. Although the trihalomethane concentration following treatment with carbon was much less than the incoming amount, the trihalomethane concentration went up again in the system, presumably because the precursors for trihalomethane formation were still present in the water and were continuing to react with chlorine. At water utility 6

the trihalomethane concentration was 3 µg/1 in the raw water, 23 µg/1 before carbon treatment, 5 µg/1 following carbon treatment, and 15 µg/1 in the distribution system. At water utility 7, the concentration was 1 µg/1 in the raw water, 47 µg/1 before carbon treatment, 9 µg/1 after carbon treatment, and 97 µg/1 in the distribution system.

Based on the foregoing results, it is apparent that those water utilities that derive their water from a well protected ground water source, or a lake, or a well protected impoundment should have little difficulty in keeping the concentration of trihalomethanes in their finished water below 100 µg/1. Where the source is not so well protected as may be the case with many river water supplies, the concentration of trihalomethanes may be greater than 100 µg/1 about 25 percent of the time--primarily during the summer and possibly in the early part of the autumn season.

SECTION 5

BENCH-SCALE STUDIES

METHODS EMPLOYED

The purpose of the bench-scale studies was to determine which of the various commercially available adsorbents should be used in the side-by-side comparison pilot plant study of activated carbon and polymeric adsorbents. The methods used in evaluating the various adsorbents included adsorption isotherm tests and small-column studies.

An adsorption isotherm is the relationship between the solute uptake expressed as the amount adsorbed per unit weight of adsorbent and the equilibrium concentration of the solute remaining in solution at a given temperature. An adsorption isotherm usually can be linearized by plotting the log of the uptake versus the log of the equilibrium concentration. This procedure was effective in linearizing the data obtained in this study.

A column study is an adsorption test made on a bed of the granular adsorbent. The relationship between the concentration of the solute in the effluent from the column and the service time of the column is called a breakthrough curve. The breakthrough curve is usually an S-shaped curve.

The solutes used in the study included chloroform, a known carcinogen; humic and fulvic acids, natural products found in water which are precursors for the formation of the trihalomethanes; and methylisoborneol (MIB), a compound that has an earthy-musty odor in water at a threshold odor concentration of about 0.1 µg/l.

The adsorbents included both granular activated carbon and polymeric adsorbents. The granular activated carbons included products prepared from both bituminous and lignite coal. The polymeric adsorbents included phenol-formaldehyde resins with amine functional groups, a styrene-divinylbenzene resin, an acrylic resin, and a carbonaceous resin adsorbent.

ADSORPTION ISOTHERMS

The Freundlich equation [6] provides a satisfactory correlation for an adsorption isotherm that can be linearized by plotting the log of the uptake, q, versus the log of the equilibrium concentration, C:

$$q = k\, C^{1/n}$$

The constants k and n for the Freundlich isotherm for humic acid, MIB, and chloroform removal for several adsorbents are given in Table 2.

The performance of the various adsorbents may be compared most easily by computing the relative effectiveness of the adsorbents in reducing the concentration of the solute to a given equilibrium value. The relative effectiveness of an adsorbent is calculated by dividing the uptake for the test carbon by the uptake for a reference carbon and multiplying the quotient by 100 percent. Table 3 contains the relative effectiveness for a number of the carbons and resins that were tested for humic acid removal, MIB removal, and MIB removal in the presence of humic acid.

The results shown in Table 3 indicate that the Calgon and ICI carbons provided a somewhat greater uptake of humic acids than the Westvaco carbon but the Westvaco carbon provided a somewhat greater uptake of MIB than either the Calgon or the ICI carbon. It is also apparent that the carbonaceous resin, Ambersorb XE 340, was not effective for the uptake of large molecules such as humic acids and that the phenol-formaldehyde resin was not effective for the uptake of small molecules such as MIB. The activated carbons on the other hand were effective for both large and small molecules.

The phenol-formaldehyde resin had about the same capacity for humic acid removal as the activated carbon. The Ambersorb XE 340 had substantially less capacity for MIB removal than any of the activated carbons. Ambersorb XE 340 was about 40 percent more effective than HD 4000 for chloroform removal at an equilibrium concentration of 10 µg/l, however.

COLUMN STUDIES

The column studies were made with extremely shallow bed depths of adsorbent--about 3.8 cm. If the concentration of the solute is low enough, a complete S-shaped breakthrough curve can be obtained with even as shallow a bed depth as that. At low concentrations, the solute can diffuse deep into the adsorbent particle and utilize a reasonably large part of its adsorption capacity before the effluent concentration has increased to 50 percent of the influent concentration.

If the concentration of the solute is high enough, the breakthrough curve may be incomplete--the part of the curve below the inflection point may be very short and the curve will therefore appear to be parabolic in form. Effectively, the solute may only diffuse a short distance into the adsorbent particle before the inflection point of the curve is reached. Thus, only a small part of the adsorption capacity may be utilized before the effluent concentration has become greater than half of the influent concentration.

The breakthrough curve can be linearized by plotting $-\ln\left[(C_o/C) - 1\right]$ versus t [7] where:

C_o = influent concentration

TABLE 2. FREUNDLICH CONSTANTS* FOR SEVERAL ADSORBENTS

Solute	Adsorbent	k	n
Humic Acid†	Calgon Filtrasorb 400	37.5	1.79
	Westvaco WVG	27.6	1.49
	ICI HD 4000	41.4	2.49
	Phenol-Formaldehyde Resin	27.3	1.10
MIB‡	Calgon Filtrasorb 400	104.7	1.94
	Westvaco WVG	112.6	2.01
	ICI HD 4000	41.9	2.23
	Rohm & Haas Ambersorb XE 340	20.8	2.24
MIB + HA§	Calgon Filtrasorb 400	78.1	1.88
	Westvaco WVG	118.9	1.80
	ICI HD 4000	70.6	1.93
	Rohm & Haas Ambersorb XE 340	21.8	2.24
Chloroform**	ICI HD 4000	7.8	1.44
	Rohm & Haas Ambersorb XE 340	18.2	1.24

* Based on q expressed as mg/gm and C expressed as mg/l.

† Based on an equilibrium humic acid concentration ranging from 0.1 to 10 mg/l.

‡ Based on an equilibrium concentration of MIB ranging from 0.1 to 10 µg/l.

§ Based on an equilibrium concentration of MIB ranging from 0.1 to 10 µg/l with an initial concentration of 10 mg/l of humic acid.

** Based on an equilibrium concentration of chloroform ranging from 4 to 300 µg/l.

TABLE 3. RELATIVE EFFECTIVENESS OF ADSORBENTS

Adsorbent*	Humic Acid†	MIB‡	MIB + HA§
Calgon Filtrasorb 400	100	100	100
Westvaco WVG	75	115	135
ICI HD 4000	110	55	95
Rohm & Haas Ambersorb XE 340	0	25	50
Phenol-Formaldehyde Resin	75	0	0

* Calgon Filtrasorb 400 is used as the reference carbon in this table.

† Based on 1.0 mg/l of humic acid (HA) as an equilibrium concentration.

‡ Based on 10 µg/l of MIB as an equilibrium concentration.

§ Based on 10 µg/l of MIB as an equilibrium concentration with an initial concentration of 10 mg/l of humic acid.

C = effluent concentration,

t = service time.

The intercept on the time axis, t', is a function of the adsorption capacity:

$$t' = Nx/vC_o$$

where:

N = an adsorption capacity coefficient,

x = the amount of adsorbent,

v = the rate of solution application.

In the column studies, x was 2 gm and v was 6.5 gpm/ft^2 (2.1 liters/hr through a column 1.3 cm in diameter).

With such short columns is it apparent that only a fraction of the total column capacity will be utilized. The percentage, P, of the available column capacity that was utilized can be computed as:

$$P = 100\ N/q$$

where q is the adsorption capacity (uptake corresponding to the influent concentration, C_o, that was determined by the adsorption isotherm test. Table 4 shows the values of N and P for humic acid and MIB removal with several activated carbons used in the column studies.

TABLE 4. COLUMN CAPACITY FOR HUMIC ACID AND MIB

Adsorbent	Humic Acid*		MIB Solution†	
	N, mg/gm	P, percent	N, mg/gm	P, percent
Calgon Filtrasorb 400	8.7	10	--‡	--‡
Westvaco WVG	3.3	5	17.1	65
ICI HD 4000	22.0	30	8.8	80

* Influent concentration of 4.5 to 4.0 mg/l.

† Influent concentration of 54 µg/l.

‡ Not tested.

It is apparent that the humic acid penetrated the ICI carbon more rapidly than it did either the Calgon or the Westvaco carbons. Although the differences are not as great, it also appears that the MIB penetrated the ICI carbon more rapidly than it did the Westvaco carbon. With a greater bed depth, the percent of the available column capacity that is utilized should approach 100 percent for each of the carbons. The difference in the rate of penetration of these two solutes into the adsorbents demonstrates that there are significant differences in the pore size distributions for these three activated carbons. The ICI carbon appears to have less pore volume in the size range used in adsorbing MIB than the Westvaco carbon has and somewhat more pore volume in the large size range used in adsorbing the humic acid.

SELECTION OF ADSORBENTS

On the basis of the adsorption isotherms and the column studies, a number of adsorbents were recommended for use in the pilot plant tests. Initially, one carbon, Westvaco WVG, was recommended for a side-by-side

comparison with polymeric adsorbents. The Westvaco carbon was recommended for use because of its good capacity for both humic substances and MIB. Later, another carbon, ICI HD 1030, was selected for inclusion in the pilot plant tests so that a lignite carbon as well as a bituminous carbon would be among the materials investigated.

No one polymeric adsorbent could be recommended as having the capacity to remove organic matter in such a wide range of molecular weights as could be removed with any of the activated carbons. Therefore, two materials were selected to be used in tandem--one an adsorbent for high molecular weight compounds such as humic acids and the other an adsorbent for low molecular weight compounds such as MIB and chloroform. Diamond Shamrock ES-561 was recommended for the humic acid removal application. This was not one of the polymeric adsorbents that was evaluated in the bench-scale tests but its properties are similar to one of the phenol-formaldehyde resins that was tested. It was expected to have reasonably low swelling properties and a fairly high capacity for humic acids in the neutral pH range. Ambersorb XE 340 was the other polymeric adsorbent recommended for the pilot plant tests; this adsorbent has a high capacity for chloroform removal.

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SECTION 6

PILOT-PLANT TESTS

PURPOSE OF THE TESTS

The primary purpose of the pilot-plant tests was to determine the performance of both activated carbon and polymeric adsorbents in adsorption columns for the removal of trace organic matter from water after these adsorbents had been subjected to repeated regeneration cycles. The pilot-plant tests were intended to provide a side-by-side comparison of both activated carbon and polymeric adsorbents to determine whether effective water treatment for trace organic removal could be obtained with either one or a combination of these adsorbents.

THE PILOT PLANT

The pilot plant was located at the Kansas City Missouri Water Treatment Plant. The water supplied to the pilot plant was water that had received virtually complete treatment including filtration. The source of the raw water is a combination of river and well water. The raw water has a pH of about 8 and a hardness ranging from about 150 to 250 mg/1 as $CaCO_3$, the water supplied to the pilot plant had a pH in the range of 10 to 11 and a hardness ranging from about 100 to 125 mg/1. Treatment includes lime softening and chemical treatment with inorganic coagulants, polymers, ammonia, potassium permanganate, and powdered activated carbon--dosages of permanganate and powdered carbon ranged from 1 to 3 mg/1 during the study period.

The pilot plant consisted of 15 glass columns with Teflon and stainless steel fittings. The columns could be operated individually or in groups of three columns connected in series to triple the bed depth. The columns were operated in a downflow mode. In the first and second phases of the study, water was applied to the columns at the rate of 2 gpm/ft^2 and the columns were filled to a depth of 3 ft with adsorbent. This provided an empty bed contact time (EBCT) of about 11.2 min. In the third and fourth phases of the study, the bed depth in some columns was less than 3 ft because some adsorbent was lost during the regeneration process--the EBCT was held constant when it was necessary to reduce the bed depth by reducing the rate of application by a corresponding amount. In the fourth phase, one set of three columns was operated at a much higher flow rate to exhaust the adsorbents more rapidly; the EBCT for each of these columns was about 2.24 min.

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ADSORBENTS

Although the original purpose of the pilot-plant test was to make a side-by-side comparison of one activated carbon and a combination of two polymeric adsorbents, the investigators did ultimately include a much larger number of granular materials in the test. The granular materials tested included:

Westvaco WVG--a bituminous base activated carbon,

ICI HD 1030--a lignite base activated carbon,

Union Carbide LCK--a petroleum base activated carbon,

American Norit ROW 0.8--a peat base activated carbon,

Calgon (new product)--an activated carbon with enhanced properties for trihalomethane removal,

Diamond Shamrock ES-561--a weak base anion exchange resin,

Diamond Shamrock A-162--a strong base anion exchange resin,

Rohm & Haas IRA 904--a strong base anion exchange resin,

Rohm & Haas XE 340--a carbonaceous resin with a good capacity for trihalomethane removal,

Filter Sand

Table 5 indicates the way the various columns in the pilot plant were loaded during each phase of the study.

TTHM AND TOC REMOVAL

The influent and effluent from each column was sampled at about one week intervals for the various trihalomethanes and for total organic carbon. Both the total trihalomethane (TTHM) concentration and the total organic carbon (TOC) concentration varied a great deal from week to week. The average influent concentration for TTHM and TOC in each of the four phases along with the corresponding standard deviations for these values are shown in Table 6.

The great variations in the influent concentrations of TTHM and TOC tend to obscure the trends in the development of a breakthrough curve. Figure 4 is a direct plot of the data for TTHM removal by Column 1 (Westvaco WVG) in Phase I. A three-point moving average can be used to smooth the curves and make the trends more apparent. The smoothed curves for the same data are shown in Figure 5. The development of the breakthrough curve becomes even easier to see if C/C_o for the smoothed data is plotted versus t. Figure 6 is such a plot for the same data--the typical S-shape of the breakthrough curve is readily apparent.

TABLE 5. COLUMN LOADING INFORMATION

Column Number	Phase I	Phase II	Phase III	Phase IV
1	WVG	WVG	WVG*	WVG†
2	WVG	WVG	WVG*	WVG†
3	WVG	WVG	WVG*	WVG†
4	ES-561	ES-561*	XE 340†	XE 340‡
5	ES-561	ES-561*	IRA 904	IRA 904*
6	XE 340	XE 340*	WVG	WVG
7	--§	HD 1030	HD 1030*	HD 1030†
8	--§	HD 1030	HD 1030*	HD 1030†
9	--§	HD 1030	HD 1030*	HD 1030†
10	--§	LCK	A-162	WVG*
11	--§	Calgon	WVG	WVG
12	--§	ROW 0.8	HD 1030	HD 1030*
13	--§	Sand	Sand	HD 1030
14	WVG**	WVG**	LCK	WVG
15	ES-561**	ES-561**	WVG††	WVG**

* Regenerated once.

† Regenerated twice.

‡ Regenerated three times.

§ Not in use.

** Steamed periodically.

†† Backwashed periodically.

Note: the bracketed columns were operated in series as a set of three.

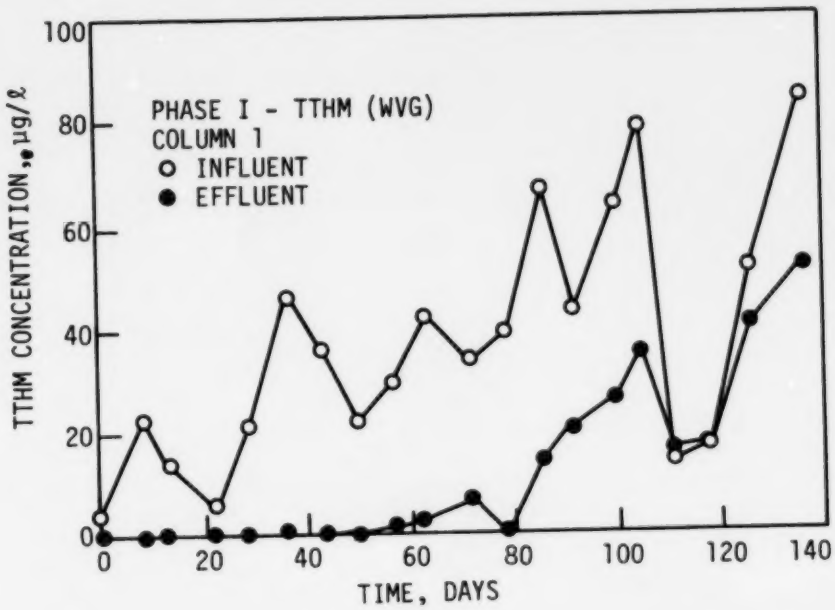

Figure 4. Direct plot of TTHM removal by Column I in Phase I.

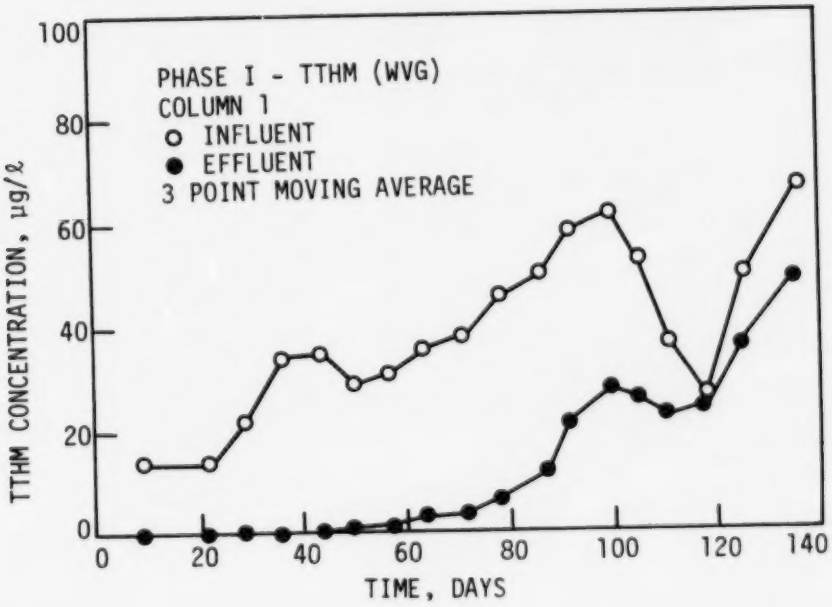

Figure 5. Smoothed curves for TTHM removal by Column I in Phase I.

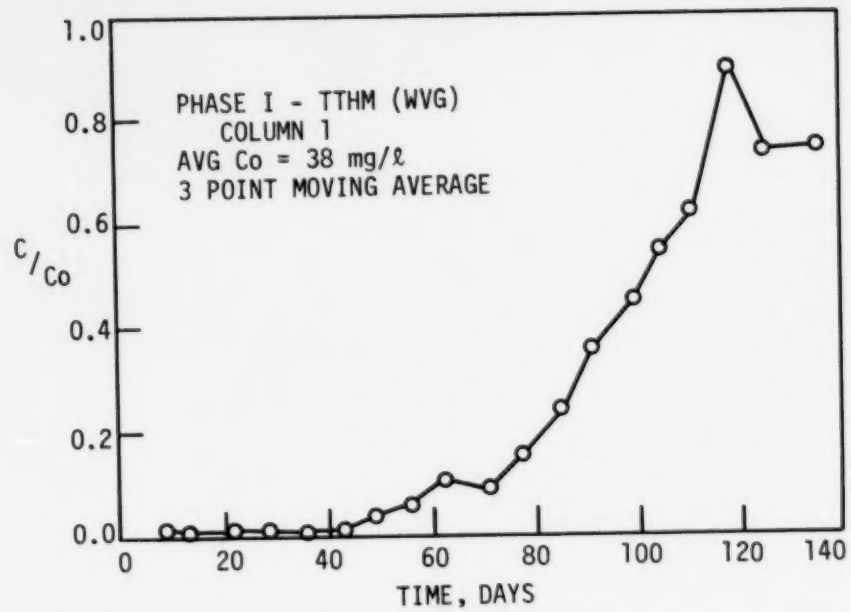

Figure 6. Breakthrough curve for TTHM removal by Column 1 in Phase I.

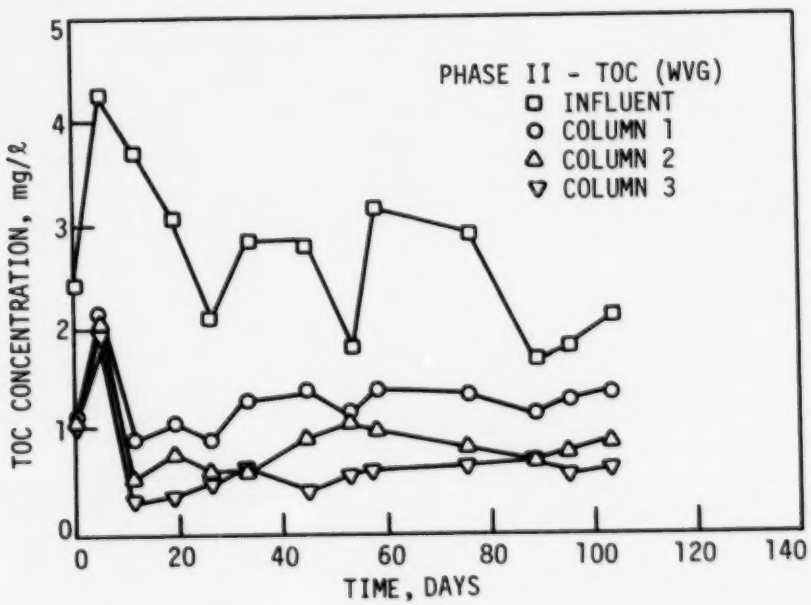

Figure 7. Direct plot of TOC removal by Columns 1, 2 and 3 in Phase II.

TABLE 6. INFLUENT TTHM AND TOC

Phase	Duration, days	TTHM, µg/l avg.	TTHM, µg/l std. dev.	TOC, mg/l avg.	TOC, mg/l std. dev.
I	183	38	24	2.5*	0.5*
II	111	68	61	2.7	0.8
III	65	13	28	3.0	0.3
IV	129	48	33	2.1	0.5

* TOC measurements began on day 92 in Phase I.

Figure 7 is a direct plot of the data for TOC removal by Columns 1, 2, and 3 (Westvaco WVG) in Phase II. Figure 8 is the smoothed version of these same curves and Figure 9 is a plot of the C/C_o data for each column. It is apparent that this concentration of TOC was too high to obtain the typical S-shaped breakthrough curve with the first 3 ft of bed depth but the additional 6 ft of bed depth provided by columns 2 and 3 has depressed the effluent concentration sufficiently so that the typical lower tail of an S-curve is apparent. The run was terminated, however, before the full S-curve could be developed.

Because the influent concentration, C_o, varied so greatly from week to week, the techniques for linearizing the breakthrough curve are not as useful with this data as they were with the data for the bench scale studies. The basic approach for estimating the adsorption capacity is still applicable, however:

$$N = \frac{v\,\overline{C}_o\,t_{0.5}}{x}$$

In this equation $\overline{C}_o$ is a time-weighted average for the influent concentration over the interval between the beginning of the run and the time, $t_{0.5}$, which corresponds to the time when the effluent concentration is half as great as the influent concentration.

Tables 7, 8, 9, and 10 indicate the values of N and $t_{0.5}$ for TTHM and TOC removal in Phases I, II, III, and IV respectively. The average capacities of the various adsorbents used in the pilot-plant studies are summarized in Table 11. The average capacities were calculated for all of the adsorbents of a given kind--virgin materials and regenerated materials

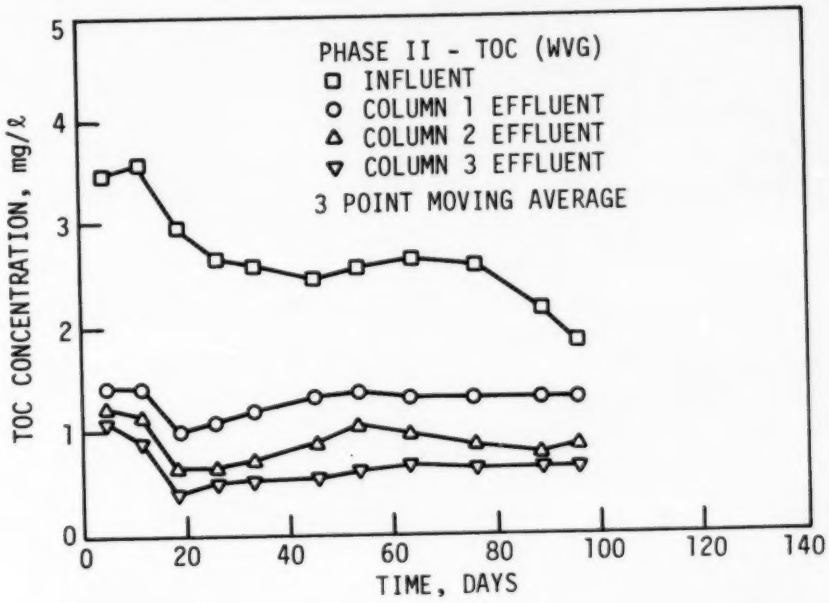

Figure 8. Smoothed curves for TOC removal by Columns 1, 2 and 3 in Phase II.

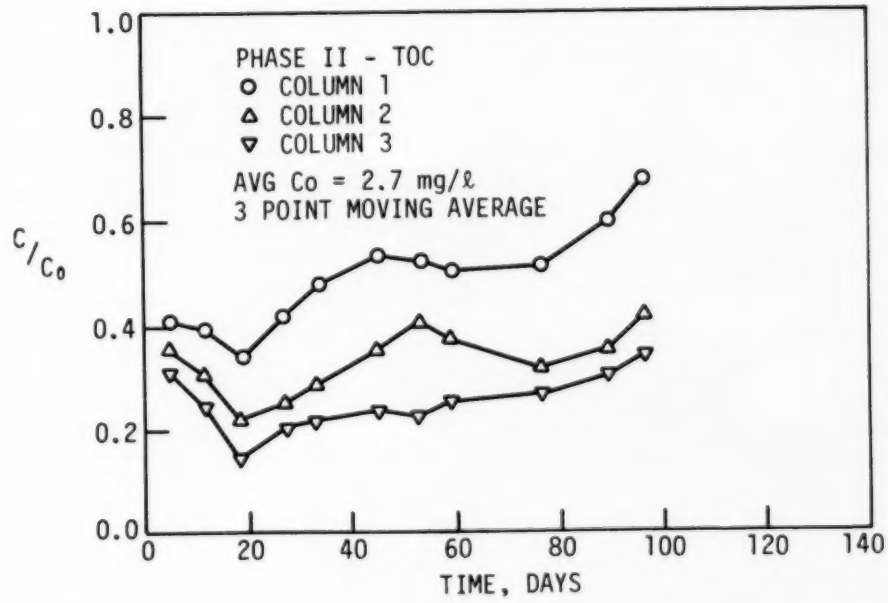

Figure 9. Breakthrough curves for TOC removal by Columns 1, 2 and 3 in Phase II.

TABLE 7. TTHM AND TOC REMOVAL IN PHASE I

Column	TTHM		TOC	
	N, mg/gm	$t_{0.5}$, days	N, mg/gm	$t_{0.5}$, days
1	0.90	92	--	--
2	1.32	180	--	--
3	--	>183	--	--
4	0.00	1	--	--
5	0.00	<1	--	--
6	>1.81	>183	--	--

Note: TOC measurements did not begin until day 92 in Phase I.

TABLE 8. TTHM AND TOC REMOVAL IN PHASE II

Column	TTHM		TOC	
	N, mg/gm	$t_{0.5}$, days	N, mg/gm	$t_{0.5}$, days
1	1.6	45	44	45
2	>1.43	>111	>62	>104
3	--	>111	--	>104
4	0.39	13	0	0
5	0.02	2	0	0
6	>1.91	>111	0	0
7	2.3	53	50	34
8	>1.55	>111	32	46
9	--	>111	35	79
10	2.2	67	4	3
11	2.26	88	0	0
12	2.1	45	62	45

TABLE 9. TTHM AND TOC REMOVAL IN PHASE III

Column	TTHM		TOC	
	N, mg/gm	$t_{0.5}$, days	N, mg/gm	$t_{0.5}$, days
1	--	--	37	37
2	--	--	>32	>65
3	--	--	--	>65
4	--	--	0	0
5	--	--	7	10
6	--	--	--*	--*
7	--	--	21	17
8	--	--	21	36
9	--	--	17	44
10	--	--	0	0
11	--	--	34	40
12	--	--	10	10
13	--	--	0	0

* IRA 904 (strong base anion exchange resin) preceded WVG in series.

TABLE 10. TTHM AND TOC REMOVAL IN PHASE IV

Column	TTHM		TOC	
	N, mg/gm	$t_{0.5}$, days	N, mg/gm	$t_{0.5}$, days
1	1.15	77	69	78
2	>0.87	>129	>68	>129
3	--	>129	--	>129
4	2.00	19	0	0
5	0	0	21	5
6	(1.46)*	(16)*	--*	--*
7	1.48	85	15	18
8	>1.04	>129	9	22
9	--	>129	9	37
10	1.14	72	45	69
11	1.16	72	28	32
12	1.56	86	16	19
13	1.22	73	13	18
14	1.18	73	54	74

* IRA 904 (strong base anion exchange resin) preceded WVG in series.

TABLE 11. AVERAGE ADSORPTION CAPACITIES

Adsorbent	Capacity for TTHM, mg/gm	Capacity for TOC, mg/gm
WVG	1.2	52
HD 1030	1.6	22
LCK	2.2	4
Calgon	2.7	0
ROW 0.8	2.1	62
ES-561	0	0
IRA 904	0	14
XE 340	2.0	0

were not considered to be different materials. The effects of regeneration on four of the adsorbents are indicated in Table 12: for practical purposes, the capacity of the adsorbents was not significantly increased or decreased by regeneration.

What is apparent in these results is that some of the adsorbents were hardly challenged in the pilot plant tests and that other adsorbents were exhausted very rapidly. In Phase I, the first bed of WVG carbon (Column 1) had reached the 50 percent breakthrough value ($C/C_o = 0.5$) in 92 days and the second bed reached 50 percent breakthrough just before Phase I was terminated. Another 90 days of testing would have been needed to bring the third bed to 50 percent breakthrough.

On the other hand, both Columns 4 and 5 which contained ES-561 (the weak base anion exchange resin) reached 50 percent breakthrough in about 1 day--this indicates that the material had virtually no capacity for TTHM. In Phase II similar results can be observed except that there are also data here for TOC removal. It is apparent that the ES-561 was ineffective for both TTHM and TOC removal. The high pH (10 to 11) of the water processed in the pilot plant was probably responsible for the poor performance of this resin. At a neutral pH value, it probably would have been a more effective adsorbent for TOC. As a result of the poor performance of the ES-561 resin, the XE 340 resin in Column 6 was not protected from the humic acids and other high molecular weight compounds that the ES-561 resin was supposed to remove.

In Phases III and IV, the adsorbents in Columns 4, 5, and 6 were arranged in a much different order by the investigators--not the order recommended by Rohm and Haas, the manufacturer of the XE 340 resin. The XE 340 resin was put into the first column of the series (Column 4) followed by IRA 904 (Column 5) which replaced ES-561 as an adsorbent for humic substances. This was followed by WVG in Column 6. Because IRA 904 has a capacity for removing TOC, it complicated the calculation of the adsorption capacity of the WVG carbon--therefore, no capacity for TOC removal is reported for the WVG carbon in Column 6 in Phases III and IV.

It has been noted in Table 10 that the TTHM capacity of the WVG carbon in Column 6 is 1.46 mg/gm whereas the WVG in Column 11 had a capacity of 1.16 mg/gm. Thus, the capacity of the WVG in Column 6 was 25 percent higher than that of the same material in Column 11. Again, this is the result of the way Columns 4, 5, and 6 were loaded. The XE 340 was removing the TTHM from the water being supplied to the three columns; the IRA 904 was removing TOC but it was producing TTHM. Presumably humic substances accumulating in the IRA 904 were being affected by the chlorine in the water so that TTHM was being formed. At any rate, TTHM was being supplied to the WVG carbon in Column 6 but the TOC level in the water had been reduced. This combination of factors apparently contributed to the differences noted in the TTHM capacity for the WVG carbon in the two columns noted.

Each of the activated carbons had a reasonably good capacity for removing TTHM from water. One activated carbon even had a higher capacity than the XE 340 resin--this was the carbon submitted by Calgon as being a special material for TTHM removal. Like XE 340, however, it had virtually no

TABLE 12. EFFECTS OF REGENERATION

Adsorbent	Adsorption Capacity, mg/gm TTHM	TOC
WVG		
virgin	1.4 (0.9-1.6)*	53 (24-69)
regen. 1x	1.1	41 (37-45)
regen. 2x	1.2	69
[average]	[1.2]	[52]
HD 1030		
virgin	1.8 (1.2-2.3)	32 (13-50)
regen. 1x	1.6	18 (16-21)
regen. 2x	1.5	15
[average]	[1.6]	[22]
XE 340		
virgin	>1.8	0
regen. 1x	>1.9	0
regen. 2x	--	0
regen. 3x	2.0	0
[average]	[2.0]	[0]
IRA 904		
virgin	0	7
regen. 1x	0	21
[average]	[0]	[14]

* Range in adsorption capacities is shown in parentheses.

capacity for TOC removal. If WVG is used as a reference adsorbent, values for the relative effectiveness can be assigned to each of the adsorbents. For TTHM removal, the relative effectiveness values are 100 for WVG, 133 for HD 1030, 183 for LCK, 225 for the Calgon carbon, 175 for ROW 0.8, 0 for ES-561, 0 for IRA 904, and 167 for XE 340. For TOC removal the values are 100 for WVG, 42 for HD 1030, 8 for LCK, 0 for the Calgon carbon, 119 for ROW 0.8, 0 for ES-561, 27 for IRA 904, and 0 for XE 340.

CONSISTENCY OF TTHM RESULTS

Some indication of the consistency of the TTHM results can be obtained by determining the adsorption capacity for chloroform and for the bromomethane compounds separately. This analysis of the data was made, in part, to determine whether the adsorbents tended to adsorb either the bromomethanes or the chloroform preferentially. The results for this analysis of the TTHM data for Column 1 (Westvaco WVG) are shown in Table 13.

TABLE 13. UPTAKE OF TTHM ON WVG CARBON

	Chloroform			Bromomethanes		
Phase	$t_{0.5}$, days	$\overline{C}_o$, µg/l	N, mg/gm	$t_{0.5}$, days	$\overline{C}_o$, µg/l	N, mg/gm
I	90	25	0.72	109*	6.2	0.22
II	45	95	1.37	>111†	8.6	>0.31
IV	74	41	1.05	>129‡	7.8	>0.29

* C/C_o = 0.2 at 105 days.

† C/C_o = 0.2 at 111 days.

‡ C/C_o = 0.2 at 129 days.

Note: TTHM concentration was too low during Phase III to determine N.

It is apparent that the uptake of chloroform was a function of the influent concentration during the pilot plant tests just as it was in the

adsorption isotherm tests. If a Freundlich isotherm is used to fit the chloroform data, the equation for the adsorption isotherm will be:

$$N = 4.23\ C_o^{1/2.15}$$

where:

$$r = 0.97$$

In the adsorption equation N is the uptake in mg/gm, C_o is the influent concentration in µg/l and r is the correlation coefficient.

If this equation is used to estimate the uptake of bromomethanes on the WVG carbon, the estimated uptakes would be:

Phase I	0.40 mg/gm
Phase II	0.46 mg/gm
Phase IV	0.44 mg/gm

Run II and Run IV were not long enough to establish the $t_{0.5}$ value for bromomethane uptake, but it is apparent by comparing the time to reach a C/C_o value of 0.2 that the run lengths were very close to the $t_{0.5}$ values. Thus, the uptake that was observed appears to be reasonably close to the concentration that would be predicted with the WVG-chloroform equation.

The data from Phase IV for the uptake of chloroform and the bromomethanes on XE 340 was analyzed in the same way. For chloroform:

$t_{0.5}$ = 16.5 days

$\overline{C}_o$ = 93.5 µg/l

N = 1.64 mg/gm

For the bromomethanes:

$t_{0.5}$ = 38.3 days

$\overline{C}_o$ = 13.7 µg/l

N = 0.56 mg/gm

The equation for the XE 340-chloroform equation derived from the bench-scale data was

$$q = 18.2\ C^{1/1.24}$$

Based on this equation, the expected uptake for chloroform on XE 340 would be 2.69 mg/gm and if this equation were used to estimate the uptake of bromomethanes, the uptake would be 0.57 mg/gm. These estimated values are reasonably close to the observed values--especially considering the fact that the EBCT for the column containing XE 340 was only 2.24 min in Phase IV.

EFFICIENCY OF ADSORPTION

Adsorption capacity is only one of the factors that must be considered in evaluating the performance of an adsorbent for a particular treatment application. The efficiency of the carbon bed depends on a number of factors in addition to the adsorption capacity. The efficiency of an adsorbent bed can be defined as the percent of the total bed capacity that has been utilized when the adsorption run is terminated.

In Figure 6, the breakthrough curve for TTHM removal indicates that about 10 percent of the total bed capacity would not have been utilized if the adsorption run had been terminated when C/C_o was equal to 0.5--the efficiency of the adsorption bed would have been about 90 percent. In Figure 9, the breakthrough curve for TOC removal on Column 1 (the first 3-ft depth of the WVG carbon) indicates that about 45 percent of this bed would not have been utilized if the adsorption run had been terminated when C/C_o was equal to 0.5--the efficiency of the adsorption bed would have been about 55 percent.

The efficiency of bed utilization can be increased by operating adsorption beds in series. When the adsorption run must be terminated, the first bed in the series will have the least amount of capacity that has not been utilized. When this bed is taken out of service for regeneration, the second adsorption bed becomes the first in the series and a fresh bed is added to the end of the series. In this way, the efficiency of adsorption is increased beyond what could be achieved with single bed operation.

The effects on adsorption bed efficiency of various criteria for terminating a run can be estimated by means of the equation for the breakthrough curve:

$$-\ln\left[(C_o/C) - 1\right] = K\,C_o\left[t - (Nx/vC_o)\right]$$

This equation is the basis for the linearization method that was described in section 4. The intercept, t', on the time axis is:

$$t' = Nx/vC_o$$

and the slope, b, is:

$$b = K\,C_o$$

where K is an adsorption rate coefficient.

The breakthrough curve in Figure 6 can be linearized by plotting $-\ln\left[(C_o/C) - 1\right]$ versus t as is shown in Figure 10. Based on this analysis, t' will be 103 days and b will be 0.111 $days^{-1}$. Therefore, for TTHM removal on the WVG carbon:

N = 1.25 mg/gm

K = 2900 liters/gm day

The breakthrough curve for Column 1 in Figure 9 has also been linearized as is shown in Figure 11. For this plot, t' was 55 days and b was 0.0133 $days^{-1}$. For TOC removal on the WVG carbon:

N = 47.5 gm/gm

K = 4.9 liters/gm day

It should be noted that the TOC data are so erratic that it makes the estimates of N and K relatively crude. However, the trend in the data is strong enough so that the constants will provide a useful estimate of the way that the efficiency varies with C/C_o at the end of the run.

The efficiency of an adsorption column can be estimated by integrating the area over the breakthrough curve, dividing that value by the total column capacity, and multiplying the quotient by 100 percent. Based on the equation for the breakthrough curve:

$$\text{Efficiency} = \frac{\ln\left[(C/C_o)(1 + e^{bt'})\right]}{bt'}$$

Based on the derived constants for the WVG carbon for TTHM uptake in Phase I:

For $C/C_o = 0.5$ Efficiency = 94 percent

For $C/C_o = 0.4$ Efficiency = 92 percent

For $C/C_o = 0.3$ Efficiency = 89 percent

Based on the derived constants for the WVG carbon for TOC uptake in Phase II:

For $C/C_o = 0.5$ Efficiency = 59 percent

For $C/C_o = 0.4$ Efficiency = 28 percent

For $C/C_o = 0.3$ Efficiency = 0 percent

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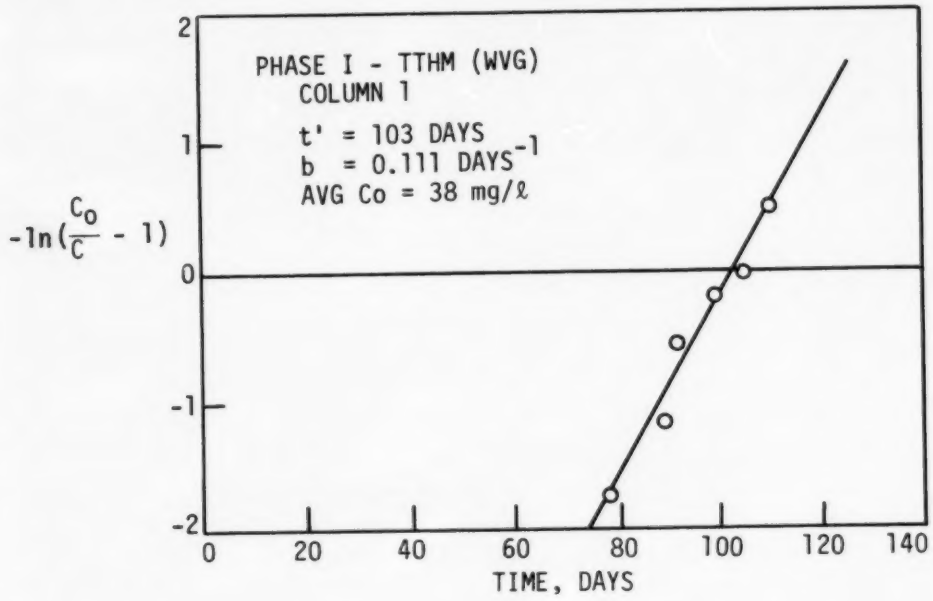

Figure 10. Linearized breakthrough curve for TTHM removal by Column 1 in Phase I.

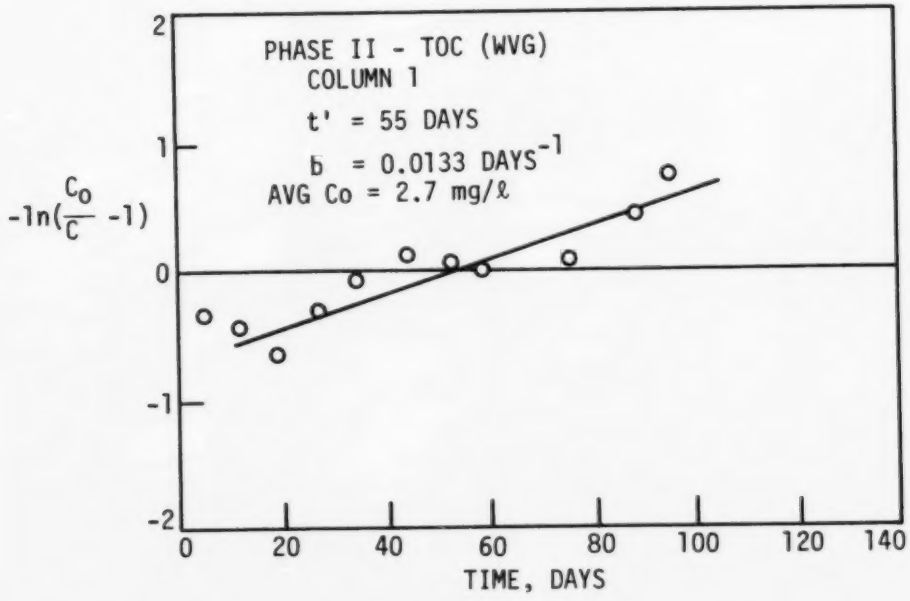

Figure 11. Linearized breakthrough curve for TOC removal by Column 1 in Phase II.

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TASTE AND ODOR

Threshold odor numbers (TON) were determined periodically during the study to determine what effect the adsorbents would have on this property of the water. In Phase I the influent and the effluent from each column were sampled 10 times. The mean TON in the influent was 2.3 with a standard deviation of 1.0--2.3(1.0). The effluent from Column 1, the first 3 ft of the WVG carbon adsorption bed, was 1.5(0.5). The effluent from Column 4, the first 3 ft of the ES-561 resin bed, was 3.1(1.3). The effluent from the second 3 ft of ES-561 was 4.0(1.9); this was also the influent to the XE 340 resin bed. The effluent from the 3-ft depth of XE 340 was 1.3(0.5). The ES-561 seemed to be producing TON which subsequently was removed by the XE 340.

The TON of the effluent was sampled five times for each column during Phase II; a sample of the influent was also obtained on the same days. With the first 3 ft of the WVG carbon the influent TON was 2.2(1.1) and the effluent was 3.0(2.8). With the resins, the influent was 2.4(0.4), the effluent from the first 3 ft of ES-561 was 2.4(0.9), from the second 3 ft it was 2.8(3.0), and from the XE 340 it was 2.0(1.0). With the first 3 ft of HD 1030 carbon, the influent TON was 2.2(1.0) and the effluent was 3.0(0.8).

The water was so highly treated by the time it reached the pilot plant that the additional removal achieved on the adsorption beds was negligible when in fact it did occur. In some cases, the adsorbents seemed to be generating TON, particularly when the adsorbent was first put into service.

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